

PCT

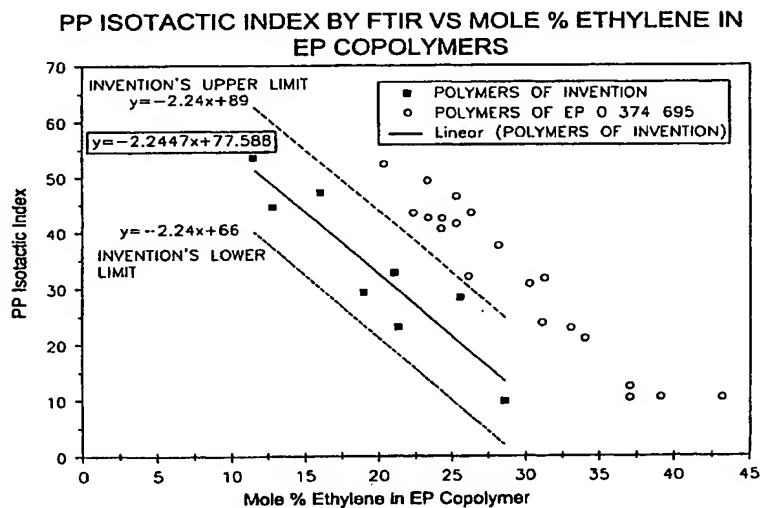
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C08F 210/16, 210/06		A1	(11) International Publication Number: WO 00/01745 (43) International Publication Date: 13 January 2000 (13.01.00)
(21) International Application Number: PCT/US99/14967 (22) International Filing Date: 1 July 1999 (01.07.99) (30) Priority Data: 09/108,772 2 July 1998 (02.07.98) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US). (72) Inventors: GADKARI, Avinash, C.; 13827 Rosebranch Court, Houston, TX 77059 (US). COZEWITH, Charles, C.; 4810 Welford Drive, Bellaire, TX 77401 (US). (74) Agents: REID, Frank, E. et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).			(81) Designated States: AU, BR, CA, CN, JP, KR, MX, RU, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PROPYLENE OLEFIN COPOLYMERS



(57) Abstract

This invention relates to propylene-olefin (PO) copolymers having unique properties described herein as a relationship of mole % olefin to: 1) isotactic index, 2) % meso propylene triad, and 3) glass transition temperature. Specifically, the isotactic index of this invention's copolymers is equal to $-0.0224O + A$ wherein O is the mole % olefin present, A is a number from 66 to 89, and the isotactic index is greater than 0. The propylene tacticity of this invention's polymers is also described by % meso triad equal to $-0.4492O + B$ wherein O is the mole % olefin present, B is a number from 93 to 100, and the % meso triad is less than 95 %. Additionally, the copolymers of this invention have a glass transition temperature equal to $-1.1082O - C$ wherein O is the mole % olefin present and C is a number from 1 to 14.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

PROPYLENE OLEFIN COPOLYMERS

FIELD OF THE INVENTION

5 This invention relates to propylene/olefin copolymers (PO) having unique properties described herein as a relationship of mole % olefin to: 1) isotactic index, 2) % meso propylene triad, and 3) glass transition temperature. The olefins include C_2 , C_4 - C_{20} alpha-olefins, the most preferred olefin being ethylene (C_2). Specifically, the isotactic index of this invention's copolymers is equal to $-0.0224O + A$ wherein
10 O is the mole % olefin present, A is a number from 66 to 89 and the isotactic index is greater than 0. The propylene tacticity of this invention's polymers is also described by % meso triad equal to $-0.4492EO + B$ wherein O is the mole % olefin present, B is a number from 93 to 100, and the % meso triad is less than 95%, preferably less than 93%, even more preferably less than 90%. Additionally, the
15 copolymers of this invention have a glass transition temperature equal to $-1.1082O - C$ wherein O is the mole % olefin present and C is a number from 1 to 14. The PO copolymers of this invention are distinguished over prior art PO copolymers by their unique crystalline characteristics coupled with elastomeric properties which make them useful in a variety of applications such as: thermoplastic elastomers (TPEs),
20 impact modifiers and compatibilizers in thermoplastic olefins (TPOs), in elastic fibers and films, in dynamically vulcanized alloys (DVAs), as curable elastomers, in adhesives, in polyvinyl chloride (PVC) replacements, and in viscosity modifiers. Due to their unique propylene crystallinity, these PO copolymers yield highly compatible blends with crystalline polypropylene (PP). These blends have superior
25 properties relative to those of blends containing crystalline PP and conventional amorphous ethylene-propylene (EP) copolymers. Furthermore, PO copolymers of this invention and their blends with polypropylene (PP) upon orientation give significantly enhanced elastic recovery and tensile strength.

30 According to another embodiment of the present invention, the PO copolymers of this invention may contain small quantities of a non-conjugated diene to aid in the vulcanization and other chemical modification. For purposes of this

invention, the term "copolymer" is intended to include both polymers formed from ethylene and one or more alpha-olefins and polymers formed from ethylene, one or more alpha-olefins, and one or more non-conjugated dienes. The preferred non-conjugated diene is selected from the group consisting of those monomers useful for vulcanization of ethylene-propylene rubbers, such as, but not limited to, 5-ethylidene--2--norbornene, 1,4--hexadiene, 1,6 octadiene, 5--methyl--1,4 hexadiene, 3,7--dimethyl--1,6--octadiene, vinylnorbornene, dicyclopentadiene or combinations thereof. The amount of diene is preferably less than 10 wt % and most preferably less than 5 wt %.

The polymers of this invention may be prepared by polymerizing a C₂, C₄-C₂₀ alpha olefin preferably ethylene and propylene in the presence of a chiral metallocene catalyst with an activator and optional scavenger.

BACKGROUND OF THE INVENTION

Metallocenes have been used to make ethylene propylene (EP) copolymers. For example, European Patent Application 128 046 discloses making an EP copolymer with at least two non-chiral metallocenes. However, achiral metallocenes are inherently incapable of making copolymers having an isotactic index greater than 0 and having the other unique crystalline characteristics coupled with elastomeric properties of EP copolymers of this invention.

EP 0 374 695 discloses the preparation of EP copolymers having an isotactic index greater than 0 using a chiral metallocene catalyst with an alumoxane co-catalyst. However, the copolymers of the present invention have an isotactic index equal to $-0.0224Et + A$ wherein Et is the mole % ethylene present, A is a number from 66 to 89, and the isotactic index is greater than 0. This relationship of mole % ethylene to isotactic index is absent in EP 0 374 695 as seen by figure 1. In general, isotactic index of EP copolymers of this invention is significantly lower than that of EP copolymers of EP 0 374 695. The low isotactic index of EP copolymers of this invention is the key to their excellent elastomeric properties.

U.S. Patent No. 5,504,172 discloses the preparation of EP copolymers having a high % meso triad tacticity of propylene units. however, % meso triad tacticity of propylene units of the copolymers of the present invention is significantly low and equal to $-0.4492Et + B$ wherein Et is the mole % ethylene present, B is a number from 93 to 100, and the % meso triad is less than 95%. This relationship of mole % ethylene to triad tacticity is seen in the polymers of U.S. Patent No. 5,504,172 as shown by figure 2. The low % meso triad tacticity of propylene units of the copolymers of the present invention is responsible for their excellent elastomeric properties.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph depicting mole % ethylene on the x-axis and isotactic index on the y-axis.

Figure 2 is a graph depicting mole % ethylene on the x-axis and % meso propylene triad on the y-axis.

Figure 3 is a graph depicting mole % ethylene on the x-axis and glass transition temperature on the y-axis.

DETAILED DESCRIPTION OF THE INVENTION

The catalyst system described below useful for making the PO copolymers of this invention is a metallocene with a non-coordinating anion (NCA) activator, and optionally a scavenging compound. Polymerization is conducted in a solution, slurry or gas phase, preferably in solution phase. The polymerization can be performed in a single- or multiple-reactor process. A slurry or solution polymerization process can utilize sub- or superatmospheric pressures and temperatures in the range of from -25 °C to 110 °C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene, alpha-olefin comonomer, hydrogen and catalyst are added. In solution polymerization, the liquid medium serves as a solvent for the

polymer. The liquid employed as the polymerization medium can be an alkane or a cycloalkane, such as butane, pentane, hexane, or cyclohexane, or an aromatic hydrocarbon, such as toluene, ethylbenzene or xylene. For slurry polymerization, liquid monomer can also be used. The medium employed should be liquid under the conditions of the polymerization and relatively inert. Preferably, hexane or toluene is employed for solution polymerization. Gas phase polymerization processes are described in U.S. Patent Nos. 4,543,399, 4,588,790, 5,028,670, all of which are herein incorporated by reference for purposes for U.S. Patent Practice. The catalyst may be supported on any suitable particulate material or porous carrier such as polymeric supports or inorganic oxide for example silica, alumina or both. Methods of supporting metallocene catalysts are described in U.S. Patent Nos. 4,808,561, 4,897,455, 4,937,301, 4,937,217, 4,912,075, 5,008,228, 5,086,025, 5,147,949, and 5,238,892, all of which are incorporated by reference for purposes of U.S. Patent Practice.

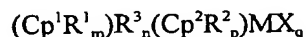
Propylene and ethylene are the preferred monomers to make the PO copolymers of the invention but ethylene may be replaced with another alpha olefin from C₄ to C₂₀.

Metallocene

The term "metallocene" and "metallocene catalyst precursor" are terms known in the art to mean compounds possessing a Group IV, V, or VI transition metal M, with a cyclopentadienyl (Cp) ligand or ligands which may be substituted, at least one non-cyclopentadienyl-derived ligand X, and zero or one heteroatom-containing ligand Y, the ligands being coordinated to M and corresponding in number to the valence thereof. The metallocene catalyst precursors are generally require activation with a suitable co-catalyst (referred to as activator) in order to yield an active metallocene catalyst which refers generally to an organometallic complex with a vacant coordination site that can coordinate, insert, and polymerize olefins.

Preferable metallocenes are cyclopentadienyl (Cp) complexes which have two Cp ring systems for ligands. The Cp ligands preferably form a bent sandwich

complex with the metal and are preferably locked into a rigid configuration through a bridging group. These cyclopentadienyl complexes have the general formula:



5

Wherein Cp^1 of ligand $(\text{Cp}^1\text{R}^1_m)$ and Cp^2 of ligand $(\text{Cp}^2\text{R}^2_p)$ are preferably the same, R^1 and R^2 each is, independently, a halogen or a hydrocarbyl, halocarbyl, hydrocarbyl-substituted organometalloid or halocarbyl-substituted organometalloid group containing up to 20 carbon atoms, m is preferably 1 to 5, p is preferably 1 to 5, and preferably two R^1 and/or R^2 substituents on adjacent carbon atoms of the cyclopentadienyl ring associated there with can be joined together to form a ring containing from 4 to 20 carbon atoms, R^3 is a bridging group, n is the number of atoms in the direct chain between the two ligands and is preferably 1 to 8, most preferably 1 to 3, M is a transition metal having a valence of from 3 to 6, preferably from group 4, 5, or 6 of the periodic table of the elements and is preferably in its highest oxidation state, each X is a non-cyclopentadienyl ligand and is, independently, a hydrocarbyl, oxyhydrocarbyl, halocarbyl, hydrocarbyl-substituted organometalloid, oxyhydrocarbyl-substituted organometalloid or halocarbyl-substituted organometalloid group containing up to 20 carbon atoms, q is equal to the valence of M minus 2.

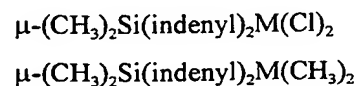
20

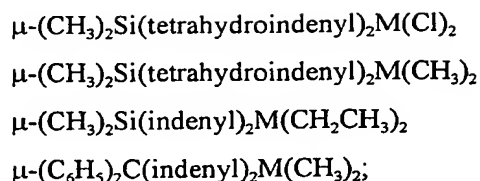
Numerous examples of the biscyclopentadienyl metallocenes described above for the invention are disclosed in U.S. Patents 5,324,800; 5,198,401; 5,278,119; 5,387,568; 5,120,867; 5,017,714; 4,871,705; 4,542,199; 4,752,597; 5,132,262; 5,391,629; 5,243,001; 5,278,264; 5,296,434; and 5,304,614, all of which are incorporated by reference for purposes of U.S. Patent Practice.

25

Illustrative, but not limiting examples of preferred biscyclopentadienyl metallocenes of the type described in group 1 above for the invention are the racemic isomers of:

30





5 Wherein m is chosen from a group consisting of Zr, Hf, or Ti.

Non-coordinating anions

10 As already mentioned the metallocene or precursor are activated with a non-coordinating anion. The term "non-coordinating anion" means an anion which either does not coordinate to said transition metal cation or which is only weakly coordinated to said cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" non-coordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the

15 anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral four coordinate metallocene compound and a neutral by-product from the anion. Non-coordinating anions useful in accordance with this invention are those which are compatible, stabilize the metallocene cation in the sense of balancing its ionic charge, yet retain sufficient lability to permit displacement by an

20 ethylenically or acetylenically unsaturated monomer during polymerization. Additionally, the anions useful in this invention are preferably large or bulky in the sense of sufficient molecular size to largely inhibit or prevent neutralization of the metallocene cation by Lewis bases other than the polymerizable monomers that may be present in the polymerization process. Typically the anion will have a molecular

25 size of greater than or equal to 4 angstroms.

 Descriptions of ionic catalysts for coordination polymerization comprised of metallocene cations activated by non-coordinating anions appear in the early work in EP-A-0 277 003, EP-A-0 277 004, U.S. Patents 5,198,401 and 5,278,119, and WO 92/00333. These teach a preferred method of preparation wherein metallocenes

30 (bisCp and monoCp) are protonated by an anionic precursors such that an alkyl/hydride group is abstracted from a transition metal to make it both cationic

and charge-balanced by the non-coordinating anion. The use of ionizing ionic compounds not containing an active proton but capable of producing both the active metallocene cation and a non-coordinating anion is also known. See, EP-A-0 426 637, EP-A- 0 573 403 and U.S. Patent 5,387,568. Reactive cations other than
5 Bronsted acids capable of ionizing the metallocene compounds include ferrocenium, triphenylcarbonium, and triethylsilylium cations. Any metal or metalloid capable of forming a coordination complex which is resistant to degradation by water (or other Bronsted or Lewis acids) may be used or contained in the anion of the second activator compound. Suitable metals include, but are not limited to, aluminum,
10 gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. The description of non-coordinating anions and precursors thereto of these documents are incorporated by reference for purposes of U.S. Patent Practice.

An additional method of making the ionic catalysts uses ionizing anionic
15 pre-cursors which are initially neutral Lewis acids but form the cation and anion upon ionizing reaction with the metallocene compounds, for example tris(pentafluorophenyl) boron acts to abstract an alkyl, hydride or silyl ligand to yield a metallocene cation and stabilizing non-coordinating anion, see EP-A-0 427 697 and EP-A-0 520 732. Ionic catalysts for addition polymerization can also be
20 prepared by oxidation of the metal centers of transition metal compounds by anionic precursors containing metallic oxidizing groups along with the anion groups, see EP-A-0 495 375. The description of non-coordinating anions and precursors thereto of these documents are similarly incorporated by reference for purposes of U.S. Patent Practice.

25

Illustrative, but not limiting, examples of suitable activators capable of ionic cationization of the metallocene compounds of the invention, and consequent stabilization with a resulting non-coordinating anion include:

trialkyl-substituted ammonium salts such as;

30 triethylammonium tetraphenylborate,

- tripropylammonium tetraphenylborate,
tri(n-butyl)ammonium tetraphenylborate,
trimethylammonium tetrakis(p-tolyl)borate,
trimethylammonium tetrakis(o-tolyl)borate,
5 tributylammonium tetrakis(pentafluorophenyl)borate,
tripropylammonium tetrakis(o,p-dimethylphenyl)borate,
tributylammonium tetrakis(m,m-dimethylphenyl)borate,
tributylammonium tetrakis(p-trifluoromethylphenyl)borate,
tributylammonium tetrakis(pentafluorophenyl)borate,
10 tri(n-butyl)ammonium tetrakis(o-tolyl)borate and the like;
- N,N-dialkyl anilinium salts such as;
N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
N,N-dimethylaniliniumtetrakis(heptafluoronaphthyl)borate,
15 N,N-dimethylanilinium tetrakis(perfluoro-4-biphenyl)borate,
N,N-dimethylanilinium tetraphenylborate,
N,N-diethylanilinium tetraphenylborate,
N,N-2,4,6-pentamethylanilinium tetraphenylborate and the like;
dialkyl ammonium salts such as;
20 di-(isopropyl)ammonium tetrakis(pentafluorophenyl)borate,
dicyclohexylammonium tetraphenylborate and the like;
- and triaryl phosphonium salts such as;
triphenylphosphonium tetraphenylborate,
25 tri(methylphenyl)phosphonium tetraphenylborate,
tri(dimethylphenyl)phosphonium tetraphenylborate and the like.

Further examples of suitable anionic precursors include those comprising a stable carbonium ion, and a compatible non-coordinating anion. These include;

tropillium tetrakis(pentafluorophenyl)borate,
 triphenylmethylium tetrakis(pentafluorophenyl)borate,
 benzene (diazonium) tetrakis(pentafluorophenyl)borate,
 tropillium phenyltris(pentafluorophenyl)borate,
 5 triphenylmethylium phenyl-(trispentafluorophenyl)borate,
 benzene (diazonium) phenyl-tris(pentafluorophenyl)borate,
 tropillium tetrakis(2,3,5,6-tetrafluorophenyl)borate,
 triphenylmethylium tetrakis(2,3,5,6-tetrafluorophenyl)borate,
 benzene (diazonium) tetrakis(3,4,5-trifluorophenyl)borate,
 10 tropillium tetrakis(3,4,5-trifluorophenyl)borate,
 benzene (diazonium) tetrakis(3,4,5-trifluorophenyl)borate,
 tropillium tetrakis(3,4,5-trifluorophenyl)aluminate,
 triphenylmethylium tetrakis(3,4,5-trifluorophenyl)aluminate,
 benzene (diazonium) tetrakis(3,4,5-trifluorophenyl)aluminate,
 15 tropillium tetrakis(1,2,2-trifluoroethenyl)borate,
 triphenylmethylium tetrakis(1,2,2-trifluoroethenyl)borate,
 benzene (diazonium) tetrakis(1,2,2-trifluoroethenyl)borate,
 tropillium tetrakis(2,3,4,5-tetrafluorophenyl)borate,
 triphenylmethylium tetrakis(2,3,4,5-tetrafluorophenyl)borate,
 20 benzene (diazonium) tetrakis(2,3,4,5-tetrafluorophenyl)borate, and the like.

A particularly preferred catalyst system is $\mu\text{-(CH}_3)_2\text{Si(indenyl)}_2\text{Hf(CH}_3)_2$
 with a cocatalyst of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate.

Ethylene Propylene Copolymers

25 EP copolymers of this invention have unique properties as evidenced by the
 relationship of their isotactic index and propylene triad tacticity to their ethylene
 content. Isotactic index and triad tacticity were determined for this invention's EP
 copolymers in the manner described below.

30 Copolymers of this invention can be blended with processing oil and other
 common additives such as nucleating agents, antioxidants, fillers, etc. and fabricated
 into objects used in a variety of applications mentioned above.

Also, blends comprising the copolymers of this invention and other alpha-olefin polymers and copolymers, e.g., polypropylene, are fabricated into objects used in a variety of applications mentioned above. Generally, these blends contain processing oil and other common additives such as nucleating agents, antioxidants, fillers, etc.

Polydispersity Index

Copolymers of the invention preferably have a polydispersity index (M_w/M_n) of from 1.5 to 10, more preferably from 1.8 to 8, even more preferably from 2.0 to 5.

Isotactic Index

Polypropylene isotactic index is determined by infra-red (IR) spectroscopy. The IR spectra of polypropylene yields two observable peaks at 997 cm^{-1} and 973 cm^{-1} . The quotient of absorbance at 997 cm^{-1} divided by the absorbance at 973 cm^{-1} is a recognized measure of isotacticity. Polypropylene isotactic index is defined as this quotient multiplied by 100.

The EP copolymers made by this invention have unique crystalline characteristic as measured by isotactic index. Figure 1 is a graph depicting the relationship of isotactic index of a given copolymer to its mole % ethylene content. The data from this invention's copolymers and EPA 037659 are plotted on the graph. As shown by Figure 1, the copolymers of this invention have a lower isotactic index for any given ethylene content when compared to EPA 037659. The lower isotactic index corresponds to relatively lower crystallinity that translates into better elastomeric properties such as high tensile strength and elongation at break coupled with very good elastic recovery. Good elastomeric properties are important for some of the potential applications mentioned above.

Triad Tacticity

The term "tacticity" refers to the stereogenicity in a polymer. For example, the chirality of adjacent monomers can be of either like or opposite configuration.

The term "diad" is used to designate two contiguous monomers; three adjacent monomers are called a triad. If the chirality of adjacent monomers is of the same relative configuration, the diad is called isotactic; if opposite in configuration, it is termed syndiotactic. Another way to describe the configurational relationship is to term contiguous pairs of monomers having the same chirality as meso (m) and those of opposite configuration racemic (r).

When three adjacent monomers possess are of the same configuration, the stereoregularity of the triad is 'mm'. If two adjacent monomers in a three-monomer sequence have the same chirality and that is different from the relative configuration of the third unit, this triad has 'mr' tacticity. An 'rr' triad has the middle monomer unit having an opposite configuration from either neighbor. The fraction of each type of triad in the polymer can be determined and when multiplied by 100 indicates the percentage of that type found in the polymer.

The triad tacticity can be determined from a ^{13}C -NMR spectrum of the propylene copolymer. The ^{13}C -NMR spectrum is measured in the following manner. To measure the ^{13}C -NMR spectrum, 250-350 mg of polymer is completely dissolved in deuterated tetrachloroethane in a NMR sample tube (diameter: 10 mm) at 120° C. The measurement is conducted with full proton decoupling using a 90° pulse angle and at least a 15 second delay between pulses

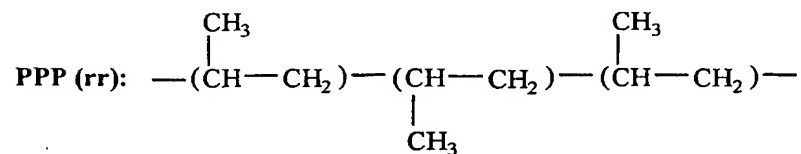
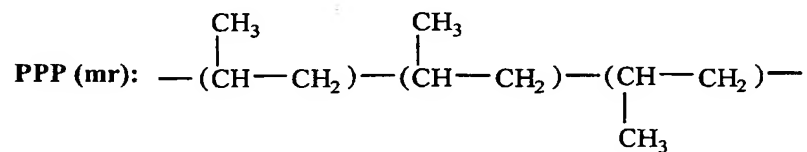
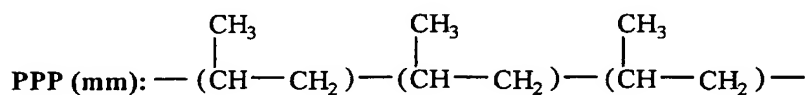
With respect to measuring the chemical shifts of the resonances, the methyl group of the third unit in a sequence of 5 contiguous propylene units consisting of head-to-tail bonds and having the same relative chirality is set to 21.83 ppm. The chemical shift of other carbon resonances are determined by using the above-mentioned value as a reference. The spectrum relating to the methyl carbon region (17.0-23 ppm) can be classified into the first region (21.1-21.9 ppm), the second region (20.4-21.0 ppm), the third region (19.5-20.4 ppm) and the fourth region (17.0-17.5 ppm). Each peak in the spectrum was assigned based on the work described in Polymer, Vol. 30 (1989) p. 1350, or Macromolecules, Vol. 17 (1984) p. 1950.

In the first region, the signal of the center methyl group in a PPP (mm) triad is located.

In the second region, the signal of the center methyl group in a PPP (mr) triad and the methyl group of a propylene unit whose adjacent units are a propylene unit and an ethylene unit resonates (PPE-methyl group).

In the third region, the signal of the center methyl group in a PPP (rr) triad and the methyl group of a propylene unit whose adjacent units are ethylene units resonate (EPE-methyl group).

PPP (mm), PPP (mr) and PPP (rr) have the following three-propylene units-chain structure with head-to-tail bonds, respectively.



The triad tacticity (mm fraction) of the propylene copolymer can be determined from a ^{13}C -NMR spectrum of the propylene copolymer and the following formula:

$$\text{mm Fraction} = \frac{\text{PPP (mm)}}{\text{PPP (mm)} + \text{PPP (mr)} + \text{PPP (rr)}}$$

The peak areas used in the above calculation are not measured directly from the triad regions in the CNMR spectrum. The intensities of the mr and rr triad regions need to have subtracted from them the areas due to EPP and EPE sequencing, respectively. The EPP area can be determined from the signal at 30.8 ppm after subtracting from it one half the area of the sum of the signals between 26 and 27.2 ppm and the signal at 30.1 ppm. The area due to EPE can be determined from the signal at 33.2 ppm.

In addition to the above adjustments to the mr and rr regions for the presence of EPP and EPE other adjustments need to be made to these regions prior to using the above formula. These adjustments are needed to account for signals present due to non-head-to-tail propylene additions. The area of the mr region may be adjusted by subtracting one half of the area between 34 and 36 ppm and the area of the rr region may be adjusted by subtracting the intensity found between 33.7 and 40.0 ppm. Therefore, by making the above adjustments to the mr and rr regions the signal intensities of the mm, mr and rr triads can be determined and the above formula applied.

The EP copolymers made by this invention have unique propylene tacticity as measured by % meso triad. Figure 2 is a graph depicting the relationship of % meso triad of a given copolymer to its mole % ethylene content. The data from this invention's copolymers and U.S. Pat. No. 5,504,172 are plotted on the graph. As shown by figure 2, the copolymers of this invention have a lower % meso triad for any given ethylene content when compared to U.S. Pat. No. 5,504,172. The lower content of % meso triads corresponds to relatively lower crystallinity that translates into better elastomeric properties such as high tensile strength and elongation at break coupled with very good elastic recovery. Good elastomeric properties are important for some of the potential applications mentioned on page 1.

Copolymer Properties

Various techniques were used to characterize the copolymers of this invention some of which are described in "Structure Characterization" The Science

and Technology of Elastomers, F. Eirich, editor, Academic Press 1978, Chapter 3 by G. Ver Strate which is incorporated by reference for purposes of U.S. Patent Practice.

5 Glass transition temperature (T_g) of polymer is usually measured by differential scanning calorimetry (DSC). The T_g of EP copolymers reported in this application is determined by either modulated DSC (MDSC) technique or conventional DSC technique.

10 The copolymer of the invention preferably has a reactivity ratio product ($r_1 \times r_2$) equal to or less than 2.5.

Conventional DSC Technique: DSC has a standard protocol of loading a calorimeter at 20 °C with a specimen free of molding strains, cooling the sample to -75 °C, scanning to 180 °C at 10 °C/min., cooling to -75 °C, and re-running the scan.
15 The T_g and melting point (T_m) are evaluated.

Modulated DSC Technique: Thermal analyzer instruments' model 2910 is used. 5-10 mg of polymer sample is loaded in the instrument at ambient temperature. The general analysis procedure calls for subjecting the sample to the following thermal segments in the order given below:
20

1. From room temperature, ramp 10 °C/minute to -60 °C.
2. Isothermal for 1.0 minute.
3. Simultaneously modulate +/- 1.0 °C every 60 seconds and ramp 5 °C/minute
25 to 150 °C.
4. Isothermal for 1.0 minute.
5. Ramp 5 °C/minute to -10 °C.
6. Isothermal for 1.0 minute.
7. Ramp 10 °C/minute to 150 °C.
- 30 8. Ramp 10 °C/minute to 25 °C.

Data is acquired and analyzed using Thermal Analyzer Instruments' Model 2200 computer and the T_g , Melting Point (T_m) and Crystallization Point (T_c) are evaluated.

High-Temperature GPC (HT-GPC)

5

SCOPE

Gel permeation chromatography (GPC) is a liquid chromatographic technique which separates macromolecules according to their hydrodynamic size. It is employed here to obtain the molecular weight distribution of polyolefin samples (e.g., PE and PP). A dilute solution of the polyolefin in a good solvent (1,2,4-trichlorobenzene, TCB) is carried through a series of separation columns filled with porous packing material (rigid particles of cross-linked styrene/divinyl benzene gel) using a mobile phase (also TCB) at constant flow rate. Separation occurs by repeated exchange of the polymer molecules between the bulk solvent and the pores of the packing material. The distribution of pore sizes thus determines the size range over which separation occurs, as well as the extent of separation, with large molecules eluting before smaller ones. After separation, a Differential Refractive Index (DRI) detector is used to measure polymer concentration as a function of elution time (or elution volume). A pre-established calibration curve, based on polystyrene standards, allows this raw data to be converted into concentration vs molecular weight data. The number, weight, and z-average molecular weights (M_n , M_w , and M_z , respectively) are then calculated from these results.

10
15
20

CALIBRATION

25

A set of columns are calibrated by running a series of narrow molecular weight polystyrene standards (Tosoh Corp., Japan) and recording their peak retention (elution) times. A total of 16 PS standards are used, covering a molecular weight range of $M_{PS} = 500-5,000,000$. PE and PP molecular weight vs retention time data are calculated from these results by assigning PE- or PP-equivalent

molecular weights for each PS standard. Final calibration curves for PE and PP then consist of 3rd-order polynomial fits of these data sets.

For PP, the "universal calibration" approach is adopted, in which $M_{PS}[\eta]_{PS}$
5 $= M_{PP}[\eta]_{PP}$ is assumed to hold. The following Mark-Houwink coefficients are employed in the relation $[\eta] = kM^\alpha$:

	$k(\text{dL/g})$	α
PS	1.75×10^{-4}	0.67
PP	8.33×10^{-4}	0.80

RUN CONDITIONS

10 INSTRUMENT: Waters 150-C GPC
COLUMNS: 3 Shodex AT-806MS (mixed bed)
MOBILE PHASE: filtered TCB, 300 ppm antioxidant (Santonox)
TEMPERATURE: 145 °C (column and injector compartments)
RUN TIME: 50 minutes
15 INJECTION VOLUME: 300 μL
FLOW RATE: 1.0 mL/min
DRI SENSITIVITY: 256
DRI SCALE FACTOR: 16

SAMPLE PREPARATION

20 4-6 mg of polymer is weighted into a 4 mL WISP vial, sufficient TCB is added to yield a concentration of 1.5 mg/mL, and the vial is capped with a PTFE septum and labeled with the work request number. Preferably, TCB from a single source is used for both sample preparation and the mobile phase to minimize
25 instability in the DRI signal as the lowest molecular weight components elute (i.e., "solvent mis-match" peaks). The sample is placed in the shaker oven at 160-170 °C

for 3-4 hours while continuously agitating at a rate of 120-160 rpm. After discarding samples that contain undissolved gel or solid particles, the vials are transferred to a pre-heated sample carousel, and the carousel quickly placed into the heated injector compartment of the GPC. The set of samples are run according to the directions for normal operation in the waters 150-C GPC manual.

DATA ACQUISITION AND ANALYSIS

Data is acquired and analyzed using Waters "Expert Ease" software. Samples are identified by the work request and customer notebook numbers. For a given chromatogram, a linear baseline is established based on the pre-peak trend, and the limits for peak integration are set by estimating the points of initial and final deviation of the signal from that baseline (and excluding "solvent mis-match" or "injection" peaks). The established calibration curve, appropriate for PE or PP, is used to convert the DRI signal vs retention time data to molecular weight distribution data. M_n , M_w , M_z , and recovered mass (relative to the control sample) are calculated by the software. A report is generated that includes these values, a plot of the raw retention time data, and a plot of the molecular weight distribution. A "time slice" report is also available.

The EP copolymers made by this invention have unique properties as measured by T_g . Figure 3 is a graph depicting the relationship of T_g of a given copolymer to its mole % ethylene content. The data from this invention's copolymers are plotted on the graph.

EXAMPLES 1-3

The polymers of Examples 1-3 were made with the following general procedure. Polymerizations were carried in a one liter stirred reactor with continuous flow of feeds to the system and continuous withdrawal of products. Solvent, including hexane, and monomers including ethylene and propylene were purified over beds of alumina and mole sieves. Toluene for preparing catalyst

solutions was also purified by the same technique. All feeds were pumped into the reactors by metering pumps except for the ethylene which flowed as a gas under its own pressure through a mass flow meter/controller. Reactor temperature was controlled by circulating water through a reactor cooling jacket. The reactor was maintained at a pressure in excess of the vapor pressure of the reactant mixture to keep the reactants in the liquid phase. The reactor was operated liquid full.

Ethylene and propylene feeds were combined into one stream and then mixed with a pre-chilled hexane stream that had been cooled to at least 0 °C. A hexane solution of triisobutyl aluminum scavenger was added to the combined solvent and monomer stream just before it entered the reactor to further reduce the concentration of any catalyst poisons. A catalyst solution was prepared by dissolving $\mu\text{-Me}_2\text{Si}(\text{indenyl})_2\text{HfMe}_2$ catalyst and (N,N dimethylaniliniumtetrakis (pentafluorophenyl) borate $([\text{DMAH}]^+\text{B}(\text{pfp})_4^-)$ activator in dry toluene. This mixture of the catalyst components in toluene was pumped separately to the reactor and entered through a separate port. The product from reactor exited through a pressure control valve that reduced the pressure to atmospheric. This caused the unconverted monomers in the solution to flash into a vapor phase which was vented from the top of a vapor liquid separator. The liquid phase, comprising mainly polymer and solvent, flowed out the bottom of the separator and was collected for polymer recovery. Polymer was recovered from solution by either steam stripping following by drying, or by solvent evaporation under heat and vacuum. Below, Table 1 shows polymerization conditions for Examples 1-3.

TABLE 1

Example #	Polymzn Temp. (C)	Feed Rates (gm/hr)				Polymzn. Time (min)	Polymer Yield (gm)
		C ₂	C ₃	Catalyst	Scavenger		
1	70	45	335	0.00934	0.000706	30	1061
2	60	18	428	0.00934	0.000706	30	1067
3	61	45.6	502	0.00969	0.00047	20	724

EXAMPLES 4-6

The polymers of Examples 4-6 were made with the following general procedure. A 5 gallon autoclave stirred tank reactor, equipped with an external jacket for temperature control, was charged with 29 pounds of dry toluene (diluent).
5 Hexane or other inert hydrocarbon solvent may be used in place of toluene. Next, 40 grams of 25% solution of triisobutyl aluminum scavenger was charged to the reactor. The contents of the reactor were stirred and maintained at a certain initial temperature shown in table 2. Generally, ethylene (C_2) and propylene (C_3) feed lines were tied together to obtain a premixed monomer feed that is fed into the
10 reactor via a single dip tube. Alternatively, ethylene and propylene may be fed directly to the reactor through individual entry tubes. The flow rates of ethylene and propylene were adjusted to give desired C_3 / C_2 monomer ratio. A catalyst solution, containing 121 mg of $\mu\text{-Me}_2\text{Si(Indenyl)}_2\text{HfMe}_2$ and 151 mg of N,N-Dimethylanilinium tetrakis(pentafluorophenyl)boron in 100 ml of dry toluene, was
15 charged in a catalyst bomb. This bomb was a part of a catalyst delivery setup capable of delivering 15 ml of catalyst solution per addition to the reactor. Initially, 30 - 45 ml of catalyst solution was added to the reactor to induce polymerization. Additional catalyst solution is added at desired time intervals during the polymerization. Reactor pressure, temperature and C_3 & C_2 flow rates were
20 monitored throughout the polymerization run that typically lasts for 10 - 30 minutes. After a certain time period, the reactor effluent was transferred, under nitrogen pressure, to a devolatilizing unit. A continuous flow of steam was introduced in this unit for a long period of time to insure evaporation of diluent. Vacuum was usually applied to accelerate devolatilization of diluent. Copolymer floated on top of water
25 when most of the solvent was evaporated. It was isolated, dried and characterized. Reaction conditions for Examples 4-6 are shown in Table 2 below.

Table 2

Example #	Initial Reaction Temp.	Final Reaction Temp.	$\Delta t =$ Final t - Initial t	Catalyst Addition Sequence	Average C_3 / C_2 (Lb/Lb)	Polymerization time	Crude Polymer Yield
4	8° c	43° c	35° c	45 ml initially 15 ml after 4 min. Of polymerization	6.8	10 min.	~ 2 Lbs.
5	9° c	25° c	16° c	30 ml initially 15 ml after 3 min. 15 ml after 6 min. Of polymerization	6.8	10 min.	~ 2 Lbs
6	9° c	28° c	19° c	30 ml initially 15 ml after 7 min. 15 ml after 11 min. Of polymerization	13.2	20 min.	~ 2 Lbs

EXAMPLE #7

600 ml of dry toluene (diluent) was introduced in a dry, deoxygenated 1L autoclave reactor equipped with stirrer and an external jacket for temperature control. Temperature of the reactor is lowered to 0° C. From a propylene feed vessel (volume 1.1L), 120 psi (ΔP) of purified propylene gas was fed into the reactor. After equilibration of reactor pressure, 25 psi (ΔP) of purified ethylene gas was introduced into the reactor. This procedure gave a desirable C_3 / C_2 monomer ratio for the synthesis of EP copolymers containing a high amount of C_3 . The catalyst solution was prepared in a dry box and transferred into A catalyst feed tube. It contained 24 mg of $\mu\text{-Me}_2\text{Si}(\text{Indenyl})_2\text{HfMe}_2$ and 15 mg of N,N-Dimethylanilinium tetrakis(pentafluorophenyl)boron in 5 ml of dry toluene. Polymerization was induced at 0° C by injecting the catalyst solution into the reactor. Reactor pressure and temperature was monitored throughout the polymerization. A temperature jump of 9° C was observed over a period of 6 minutes after the addition of the catalyst solution. After the initial jump, the reactor temperature leveled off and decreased with increasing polymerization time. Reactor pressure decreased gradually during the polymerization. The reactor was vented completely after 20 minutes of polymerization and the contents of the reactor were poured into a beaker containing large excess of acetone. The precipitated polymer was dried under vacuum at 100° C for 24 hours. The polymer yield was 19.3 gm.

EXAMPLE #8

500 ml of dry toluene (diluent) was introduced in a dry, deoxygenated IL autoclave reactor equipped with stirrer and an external jacket for temperature control. Temperature of the reactor was lowered to -10°C . A catalyst solution containing 12 mg of $\mu\text{-Me}_2\text{Si}(\text{Indenyl})_2\text{HfMe}_2$ and 10 mg of N,N-Dimethylanilinium tetrakis(pentafluorophenyl)boron in 5 ml of dry toluene was injected in the reactor. The reactor was maintained under a slight positive pressure of dry nitrogen. Polymerization was induced at -10°C by introducing a gaseous mixture of C_3 and C_2 into the reactor. The molar ratio of $\text{C}_3:\text{C}_2$ in this mixture was 3.5:1. The flow of monomer mixture continued from the feed vessel to reactor until there is no pressure difference between the two. At this time the reactor inlet valve was shut off and polymerization was continued. Reactor pressure and temperature was monitored throughout the polymerization. A temperature jump was observed of 18°C (-10°C to 8°C) over a period of 5 minutes since the introduction of the monomer mixture in the reactor. After the initial jump, the reactor temperature leveled off and decreased with increasing polymerization time. Reactor pressure decreased gradually during the polymerization. The reactor was vented completely after 20 minutes of polymerization and the contents of the reactor were poured into a beaker containing large excess of acetone. The precipitated polymer was dried under vacuum at 100°C for 24 hours. The polymer yield was 20 gm.

TABLE 3

Example #	ID #	C13 NMR (1)				GPC (2)		FTIR (3)	DSC (4)		Tensile properties			
		Mole%	C3 triads % mm	r1 X r2		Mw	MWD		iPP	Tg (C)	Tm (C)	TS (psi)	Eb (%)	Rec (5) (%)
1	35A	28.68	83.8	0.75		118100	1.8	9.5						
2	35C	11.4	90.63	1.57		124700	1.8	54.3	-17.2	78.8				
3	39A5	18.92	88.7	0.73		149000	1.8	29.6	-27.9	44.3	2225	1490	94	
4	18758-61	21.3	89	0.85		125785	2.25	23.2	-30.5	46.3	1380	1800	92	
5	18758-62	21	89.64	0.90		187980	1.65	33.3	-32	41.8	1960	1450	82	
6	18758-63	12.72	92.5	0.78		217540	1.75	45.1	-25.7	42.8, 72	2550	1030	31	
7	17450-113-1	25.6	85.4	1.16		154045	1.7	28.6			1050	1755	77	
8	17450-125-1	16	91.07	1.33		188370	1.7	47.8						

C13 nmr

%mm C3 triads were calculated according to the procedures set forth above supplemented by the teachings of U.S. Patent 5,504,172

(1) C13 nmr: %mm C3 triads were calculated according to the procedures set forth above supplemented by the teachings of U.S. Patent 5,504,172
r1 x r2 product calculated per reference M. Kakugo, et al., Macromolecules, 15, 1150 (1982)

Both references are incorporated by reference for purposes of U.S. practice.

(2) GPC: Polypropylene calibration used

(3) FTIR iPP INDEX: Absorbance ratio at 997 / 973 cm⁻¹

Reported Tm (melting point) is for 1st melt. Samples did not crystallize within the time span of DSC test. Therefore, crystallization point was not detected. Generally, high C3 EP copolymers crystallize slowly.

Microtensile specimens were pulled at 5 inch/min. Rate in an Instron and held for 10 minutes at 150% elongation and then released.

Residual set was measured after 10 minutes. Recovery, a measure of elasticity, was calculated as follows:

% Recovery = 100 - (% set)

While the present invention has been described and illustrated by reference to particular embodiments, it will be appreciated by those of ordinary skill in the art that the invention lends itself to variations not necessarily illustrated herein. Reference should be made solely to the appended claims and their equivalents for purposes of determining the true scope of the present invention. For example, 5 fabricated products comprising the claimed copolymer of this invention are also part of this invention. Such fabricated products can also optionally comprise one or more of an alpha olefin polymer or copolymer, a processing oil, and other additives. One such particularly preferred alpha olefin polymer is polypropylene.

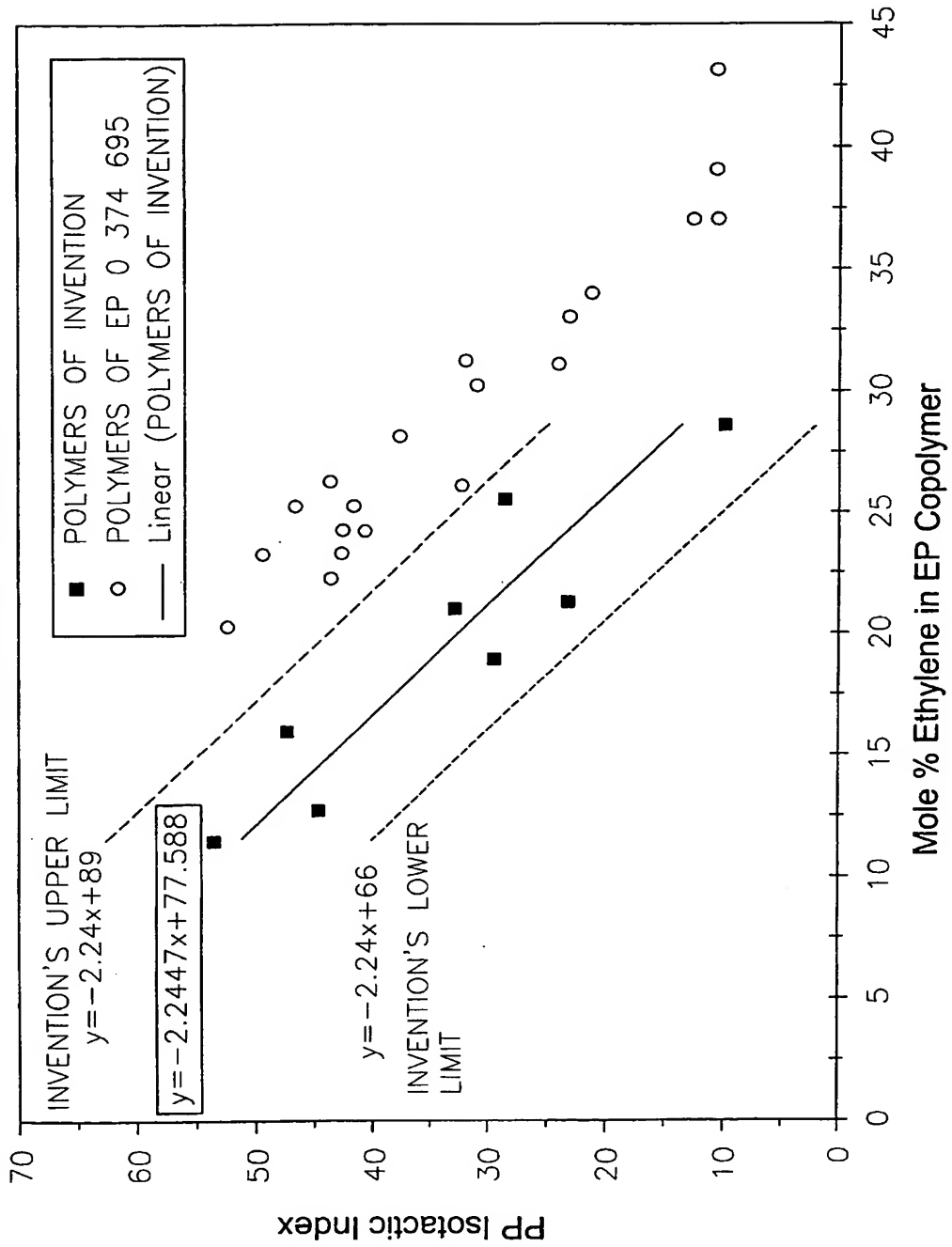
CLAIMS:

1. A propylene/olefin copolymer wherein said copolymer has:
 - (a) an isotactic index equal to $-0.0224O + A$ wherein O is the mole % olefin present, A is a number from 66 to 89, and the isotactic index is greater than 0;
 - (b) a % meso triad of equal to $-0.4492O + B$ wherein O is the mole % olefin present, B is a number from 93 to 100, and the % meso triad is less than 95%.
2. The copolymer of claim 1 wherein said olefin is ethylene.
3. The copolymer of claim 1 or 2 having a glass transition temperature equal to $-1.1082Et - C$ wherein Et is the mole % ethylene present and C is a number from 1 to 14.
4. The copolymer of any of the above claims with an ethylene content from 10 to 35 mole %.
5. The copolymer of any of the above claims with number average M_w from 15,000 to 2,000,000 and an M_w/M_n ratio from 1.5 to 10.
6. The copolymer of any of the above claims having a T_m of from 25-125° C.
7. The copolymer of any of the above claims having a reactivity ratio product ($r_1 \times r_2$) equal to or less than 2.5.
8. An article of manufacture comprising the copolymer of any of the above claims, optionally blended with one or more of other alpha olefin polymers and copolymers, processing oil, an other additives.

9. The article of claim 8 wherein said copolymer is blended with polypropylene.
10. The article of claim 8 or 9 wherein said copolymer blend is oriented.
11. A process for making the copolymer of claim 1 comprising polymerizing propylene and a C₂, C₄-C₂₀ alpha olefin with a metallocene and an activating cocatalyst.

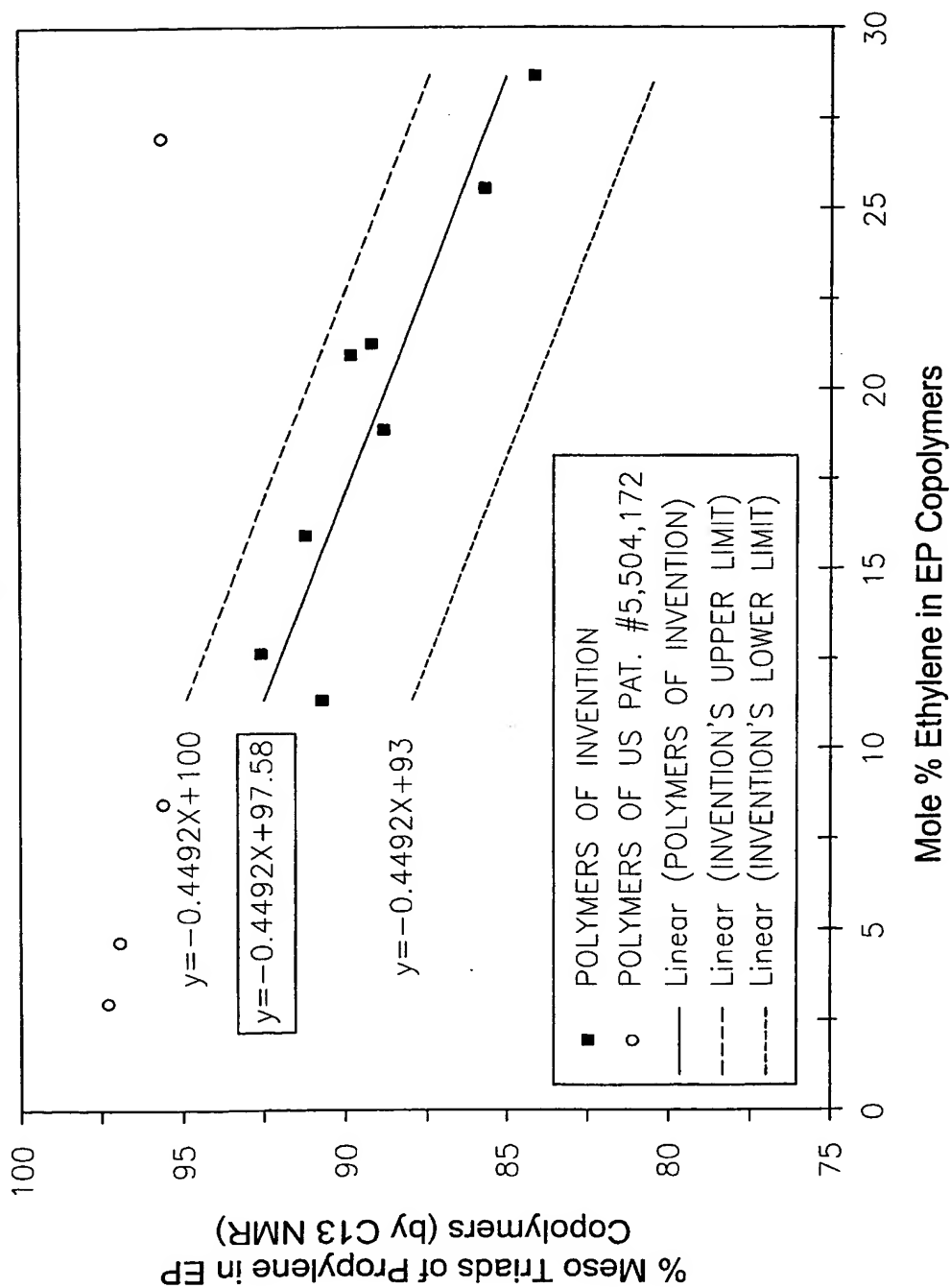
1/3

PP ISOTACTIC INDEX BY FTIR VS MOLE % ETHYLENE IN EP COPOLYMERS

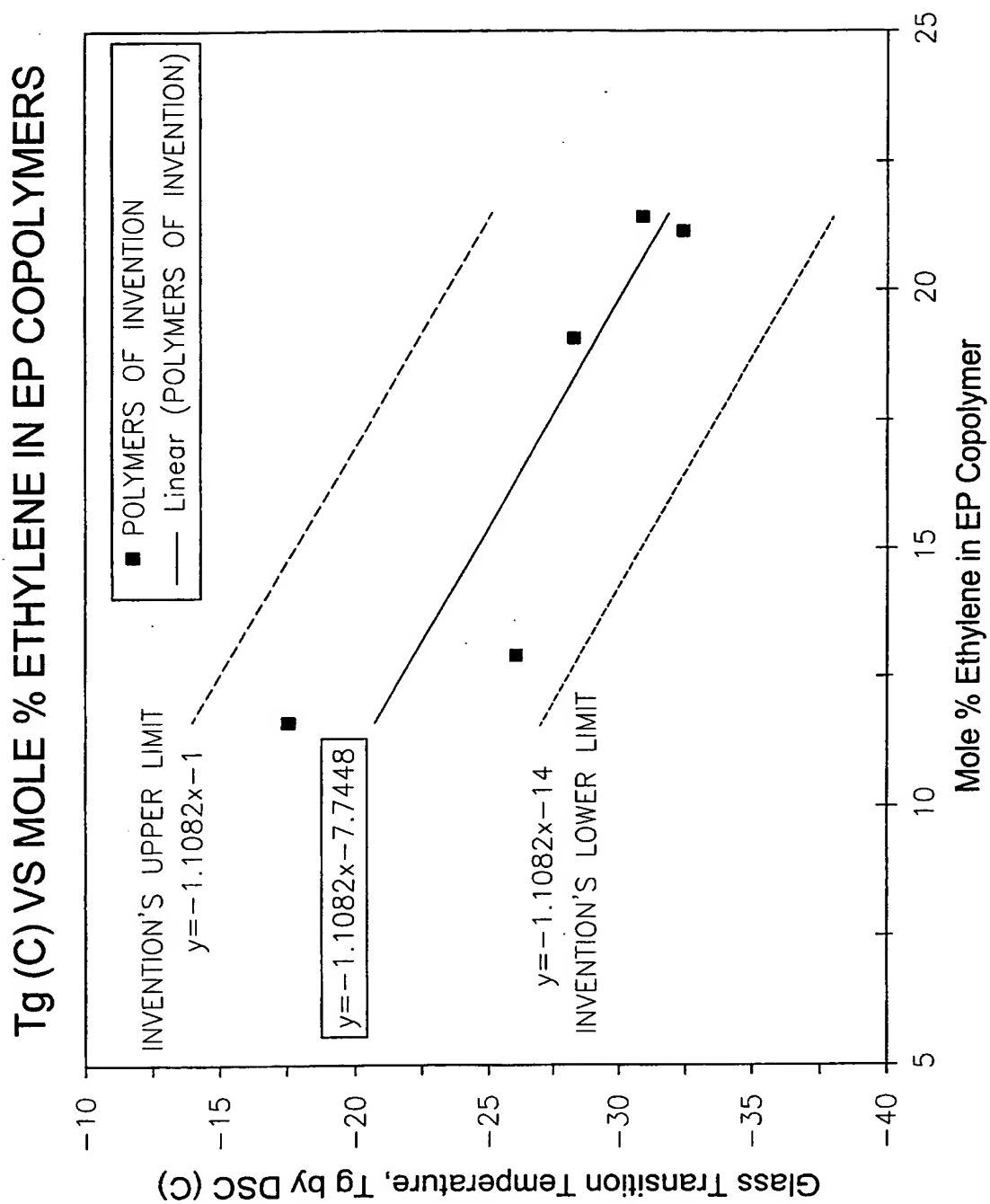


2/3

% MESO PROPYLENE TRIADS (mm) VS MOLE % ETHYLENE IN EP COPOLYMERS



3/3



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/14967

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F210/16 C08F210/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 374 695 A (POLYSAR LTD) 27 June 1990 (1990-06-27) cited in the application the whole document ---	1-11
X	US 5 504 172 A (IMUTA JUNICHI ET AL) 2 April 1996 (1996-04-02) cited in the application column 34, line 34 - line 38; claims ---	1-8, 11
X	WO 96 06132 A (D & S PLASTICS INT ;SRINIVASAN SATCHIT (US); SZCZEPANIAK EDWARD (U) 29 February 1996 (1996-02-29) page 3, line 6 - line 20 page 9, line 23 -page 11, line 3; claims --- -/--	1-11



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

26 October 1999

Date of mailing of the international search report

05/11/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Kaumann, E

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/14967

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 582 194 A (HOECHST AG) 9 February 1994 (1994-02-09) example 1 ---	1,11
X	EP 0 302 424 A (HOECHST AG) 8 February 1989 (1989-02-08) comparative example H examples 19-22 ---	1,11
X	EP 0 480 190 A (BASF AG) 15 April 1992 (1992-04-15) claim 1; example 5 ---	1
P,X	EP 0 890 584 A (CLARIANT GMBH) 13 January 1999 (1999-01-13) example 6 -----	1-7,11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/14967

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0374695 A	27-06-1990	AU 622248 B AU 4617789 A CN 1043508 A JP 2214709 A	02-04-1992 21-06-1990 04-07-1990 27-08-1990
US 5504172 A	02-04-1996	JP 7145212 A CA 2125246 A CN 1103067 A EP 0629631 A JP 8012615 A JP 7070227 A JP 8012715 A US 5739366 A US 5767033 A US 5959046 A JP 7138326 A JP 7149832 A	06-06-1995 08-12-1994 31-05-1995 21-12-1994 16-01-1996 14-03-1995 16-01-1996 14-04-1998 16-06-1998 28-09-1999 30-05-1995 13-06-1995
WO 9606132 A	29-02-1996	US 5773515 A US 5763534 A AU 3409195 A CA 2198455 A EP 0777700 A JP 10505372 T	30-06-1998 09-06-1998 14-03-1996 29-02-1996 11-06-1997 26-05-1998
EP 0582194 A	09-02-1994	AT 165832 T DE 59308494 D ES 2114978 T JP 6157661 A US 5455365 A US 5869584 A	15-05-1998 10-06-1998 16-06-1998 07-06-1994 03-10-1995 09-02-1999
EP 0302424 A	08-02-1989	DE 3726067 A AT 65510 T AU 604557 B AU 2043588 A CA 1317411 A IN 171274 A JP 1051408 A JP 2942263 B JP 10067820 A US 5661096 A US 5416178 A	16-02-1989 15-08-1991 20-12-1990 09-02-1989 04-05-1993 29-08-1992 27-02-1989 30-08-1999 10-03-1998 26-08-1997 16-05-1995
EP 0480190 A	15-04-1992	DE 4030379 A AT 123500 T DE 59105656 D ES 2073083 T JP 4234411 A	02-04-1992 15-06-1995 13-07-1995 01-08-1995 24-08-1992
EP 0890584 A	13-01-1999	DE 19729833 A JP 11100413 A	14-01-1999 13-04-1999